Influence of water on localized and delocalized molecular m

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A B S T R A C T

The influence of hydration on cellulose molecular mobility is investigated by two dielectric methods at different molecular scale. The mobility of side groups, assigned to γ mode, for dried cellulose increases. The water molecules have an anti-plasticizer effect on γ mode due to the water–polymer hydrogen bonding. For the β relaxation mode, only observed by the Thermo Stimulated Current technique, the hydration plays a role of plasticizer. The α relaxation mode assigned to the delocalized cooperative mobility of long chain segments of cellulose is plasticized by water. The study of activated parameters deduced from fractional polarization procedure, shows an increase of the activation enthalpy range with dehydration. It permits to conclude that reduction of hydrogen bonds density leading to a more extended cooperative mobility.

Keywords:
Dielectric properties, relaxation, electric modulus
Thermally stimulated and depolarization current
Polymers and organics
Hydration

[1–5]. Previous studies on biopolymers/water or hydrated polymers have demonstrated the determinant role of the hydration level on the dynamic chain [6]. But some points remain obscure as interaction of vegetal polymers with water. The aim of this work is to shed some light on the influence of this interaction and their molecular scale. One of the routes is to study the dynamic of relaxation modes determined by Dynamic Dielectric Spectroscopy and Thermo Stimulated Current technique. The synergy of both methods, and their wide range of frequency, might allow us to describe in a better way the molecular origin of the dielectric relaxation modes and to solve some problems regarding their interpretation. The molecular origin of relaxation modes and their behavior with water content at various molecular levels will be proposed and discussed.

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2. Experimental

2.1. Materials

High purity microcrystalline cellulose powder extracted from cotton linters was provided by Sigma–Aldrich Company. The cellulose powder (20 μm in diameter) was stored at 4 °C. Its water content was (4.5 ± 0.2)% w/w (loss weight after 40 days over P_2O_5). For Thermally Stimulated Current measurements, the powder was compacted (75 MPa) into thin disks (4 mm in diameter and 1 mm thickness). The so-called dehydrated samples were dried for 24 h under vacuum at 120 °C just before experiments. For Dynamic Dielectric Spectroscopy, the powder was inserted into a home-made capacitor with parallel discs of 10 mm in diameter, and compacted into 100–300 μm sheets. For dehydrated samples, the same drying procedure was applied.

2.2. Methods

2.2.1. Dynamic dielectric spectroscopy (DDS)

A Novocontrol Broadband Dielectric Spectrometer system BDS 4000 was used to obtain the dielectric relaxation map in broad temperature and frequency scales. The experiments were carried out in the frequency range of 10^{-1} to 10^{6} Hz from −150 to 200 °C by steps of 5 °C. The complex dielectric permittivity $\varepsilon_T^*(\omega)$

was recorded. Relaxation modes were described by the Havriliak–Negami function [7,8]:

$$\varepsilon_T^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{HN})^{\alpha_{HN}}\right]^{\beta_{HN}}}, \quad (1)$$

where τ_{HN} is the relaxation time of Havriliak–Negami (HN) model, α_{HN} and β_{HN} characterize the width and the asymmetry of the relaxation time distribution respectively.

2.2.2. Thermally Stimulated Current (TSC)

TSC measurements were carried out with a home-made equipment previously described [9,10]. The principle of this technique is briefly reminded: a sample is placed between two electrodes in a hermetic cell filled with dry helium. Thereafter, it is polarized with a DC field E_p during a given time t_p at the temperature T_p. The system, under the electric field, is then quenched till $T_0 \ll T_p$ assisted by liquid nitrogen: the dipoles orientation previously induced is frozen. Then, the sample is short-circuited for a given time (t_{cc}) to evacuate surface charges. Finally, the temperature is increased from T_0 to a final temperature $T_f > T_p$, at a constant heating rate q and the depolarization current I due to the return to equilibrium of dipolar units is recorded with a Keithley 642 electrometer with sensitivity of 10^{-16} A. The following parameters applied in this study are: $t_p = 2$ min, $t_{cc} = 2$ min and $q = 7$ °C/min. The temperatures T_p, T_0 and T_f were chosen according to the range of temperature in which the relaxation modes are observed.

Each elementary thermogram can be considered as a Debye process characterized by a single relaxation time $\tau(T)$. The temperature dependence of relaxation time can be determined by the following equation:

$$\tau(T) = \frac{1}{qI(T)} \int_T^{T_f} I(T)dT. \quad (2)$$

The relaxation time $\tau(T)$ of all the elementary spectra versus $1/T$ is linear and obeys to the Arrhenius–Eyring equation:

$$\tau(T) = \frac{h}{k_B T} \exp\left[-\frac{\Delta S}{R}\right] \exp\left[\frac{\Delta H}{RT}\right] = \tau_{0a} \exp\left[\frac{\Delta H}{RT}\right], \quad (3)$$

where k_B is the Boltzmann constant, R is the gas constant, h is the Planck constant, τ_0 the pre-exponential factor, ΔH the activation enthalpy and ΔS the activation entropy.

3. Results

3.1. High frequency analyses

The complex dielectric permittivity was measured by dielectric dynamic spectroscopy in an extended frequency range. Fig. 1 shows isochrones of the imaginary part of the dielectric permittivity of pristine cellulose for different frequencies from 10^{-1} to 10^6 Hz. In a last paper [11], we showed that three dielectric relaxation modes were pointed out for cellulose. At lower temperature ($T < 0$ °C), one relaxation mode was observed corresponding to γ mode. It was related to localized side group mobility of cellulose i.e. hydroxyl and hydroxymethyl ones. At around 35 °C one isothermal signal was obtained attributed to the conformational changes of confined water. At higher temperature and low frequency, the increase of dielectric loss was associated with the Maxwell–Wagner–Sillars (MWS) effect that superimposed on the high temperature mode of cellulose called α. The latter was extracted and analyzed thanks to an analytical method and assigned to cooperative delocalized mobility in the glass temperature domain of cellulose.

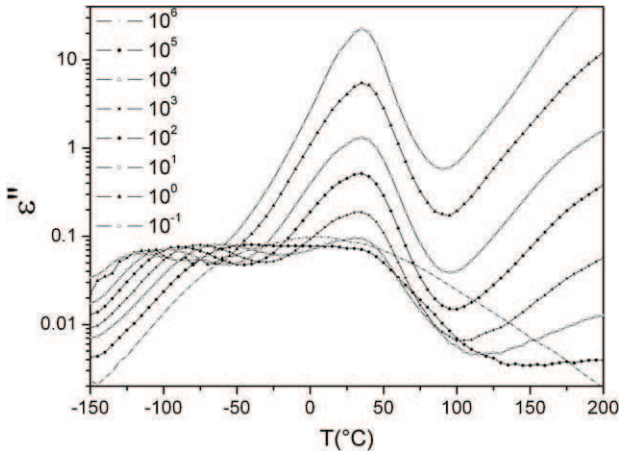


Fig. 1. Imaginary part of dielectric permittivity of pristine cellulose as a function of temperature for frequencies between 10^6 and 10^{-1} Hz.

3.1.1. γ Relaxation mode

To investigate the water influence on dielectric response, the experiments were carried out on the dried sample. The temperature dependence of the relaxation time for γ modes of hydrated (pristine) and dried cellulose was plotted in Fig. 2. In every instance, γ mode followed Arrhenius equation. However, as displayed in Fig. 2, hydrated cellulose had a more important line slope. The activation energy values of γ modes for hydrated and dehydrated cellulose are $\Delta H = 50.9 \pm 0.2$ kJ mol^{-1} and $\Delta H = 35.2 \pm 0.3$ kJ mol^{-1}, respectively. The activation energy for lower temperature relaxation mode γ of hydrated sample is more than dehydrated one. Water presence made more difficult for dipolar moments of side groups to jump over the energy barrier. The γ mode was anti plasticized by water.

3.1.2. Isothermal signal (T_{max} = 35 °C)

In order to study the isothermal signal observed by DDS near the isotherm $T = 35$ °C the real part of the dielectric permittivity was plotted in Fig. 3 for eight different frequencies (from 10^{-1} to 10^6 Hz). The strength of this isothermal mode decreased with the increase of the frequency. Its temperature maximum was frequency independent. This mode vanishes after dehydration. It

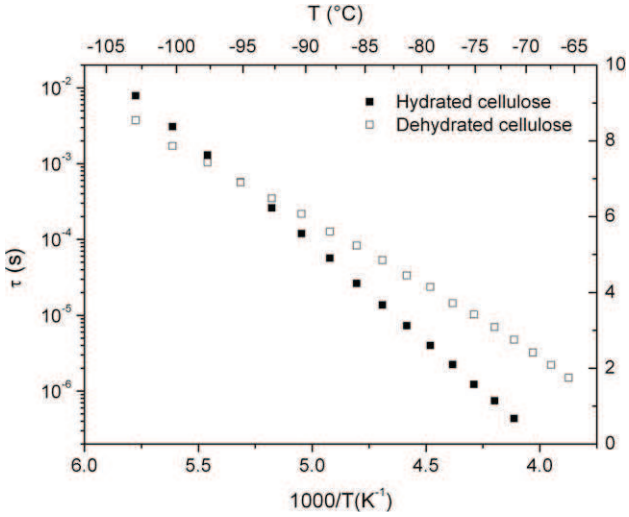


Fig. 2. Arrhenius diagram for hydrated (pristine) and dried cellulose for the low temperature (γ) relaxation mode.

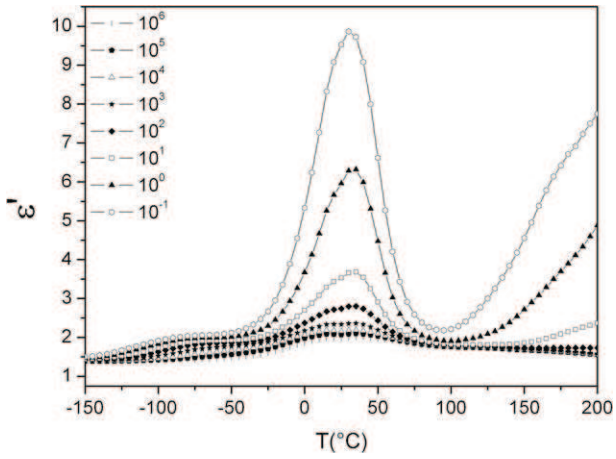


Fig. 3. Real part of dielectric permittivity of pristine cellulose as a function of temperature for frequencies between 10^6 and 10^{-1} Hz.

has been assigned to presence of the water in sample. The similar signal, related to presence of confined water, was already mentioned by other authors [12]. Moreover, the evolution of the real part of the complex permittivity values at this temperature range created a peak centered at 35 °C which is characteristic of a first order transition. Authors which studied first order transitions [12–14] pointed out the same temperature evolution of ε'. This signal corresponds to water molecules which are confined in the center of pores: free water. These molecules are strongly influenced by the ones which are linked to inner wall of pores: non-freezing water. This confined water in cellulose is a mix of free and non-freezing water molecules which both of them are located in the pores.

3.1.3. α Relaxation mode

At higher temperature, the α relaxation mode which was disturbed by the MWS effect was analyzed by applying an analytical method based on the approximation of the logarithmic derivative of the real dielectric permittivity by the dielectric loss. This convenient technique was already used in a previous paper [11]. In Fig. 4, the temperature dependence of relaxation time for hydrated and dried cellulose of α modes was reported, respectively. Both of these modes followed the Arrhenius equation. Using this equation the fit lines are calculated and showed by dash lines in Fig. 4. The activation enthalpy for dried and hydrated cellulose were, respectively $\Delta H = 96 \pm 4$ kJ mol^{-1} and $\Delta H = 76 \pm 5$ kJ mol^{-1}. The activation enthalpy for dried sample was more important. Contrary to the γ mode, the hydration of cellulose acts like a plasticizer for α mode.

3.2. Low frequency analyses

The dielectric experiments were carried out by TSC in order to increase the frequency range and to complete the DDS results. In a last work [11], we showed that three relaxation modes for cellulose were exhibited: in the low temperature range ($T < 0$ °C) γ and β modes with the maxima located at -130 ± 5 °C and -70 ± 7 °C, respectively; in the high temperature range ($T > 0$ °C) α mode with maximum at 80 ± 5 °C. The influence of hydration on these three dipolar relaxation modes was studied.

3.2.1. γ and β relaxation modes (T < 0 °C)

The low temperature modes of cellulose were strongly influenced by presence of water. To study the evolution of intensity and temperature position of the maximum of γ and β complex modes, two temperature scans were carried out for pristine and dried cellulose. These results were illustrated in Fig. 5. γ Mode which was attributed to side group mobility, was shifted to lower temperature (about 7 °C) after dehydration. Without water molecules, the molecular mobility associated with γ mode increased. In contrary to the γ mode, the molecular mobility associated with β decreased after dehydration. The β relaxation mode appeared at about 15 °C toward higher temperature. The intensities of both β and γ modes decreased for dried sample. The density of the dipolar moments susceptible to be oriented under electric field reduced owing to the decreasing of the quantity of: dipolar water molecules, of the voluminous water–polymer complex. Water molecules acted like a plasticizer for the β, an anti-plasticizer for γ mode. The results obtained for the latter one confirmed those obtained by DDS technique.

3.2.2. α Relaxation mode (T > 0 °C)

The influence of hydration on the α relaxation mode of cellulose was studied by TSC technique. The complex modes obtained for hydrated and dried sample at higher temperature were analyzed by the experimental procedure of fractional polarizations. The elementary thermograms were registered and their activation parameters were calculated. In Fig. 6, the evolution of pre-exponential factor versus the activation enthalpies of α mode for hydrated and dried cellulose was plotted. The compensation phenomenon

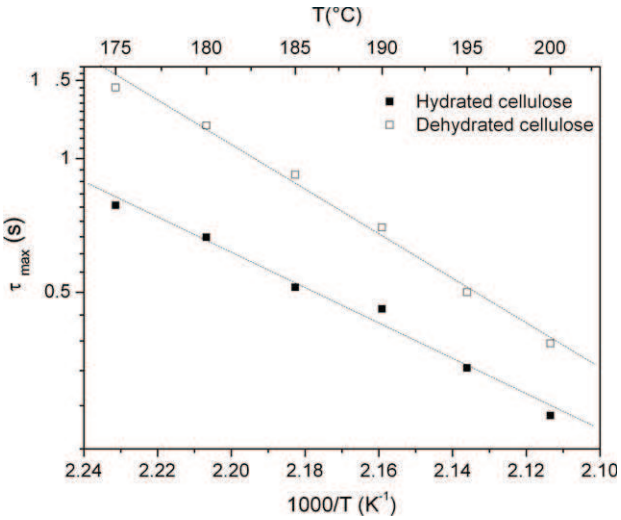


Fig. 4. Arrhenius diagram for hydrated (pristine) and dried cellulose for the high temperature (α) relaxation mode.

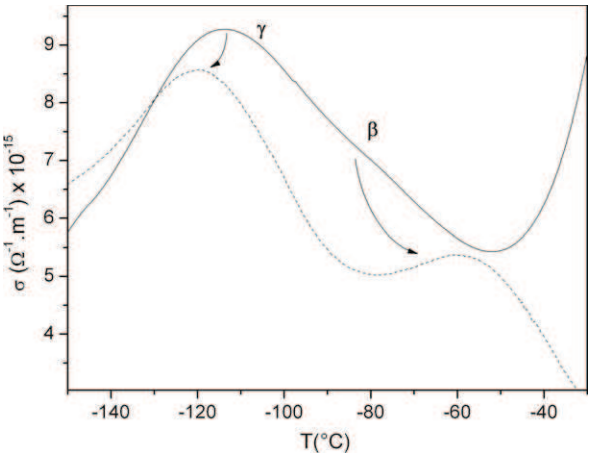
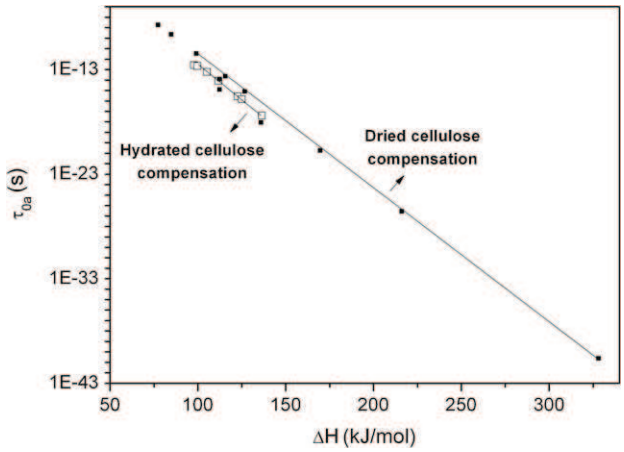


Fig. 5. Complex TSC thermograms of hydrated (solid line) and dried cellulose (dashed line) for the low temperature γ and β relaxation modes.



3. Pre-exponential factor of α mode of hydrated and dried cellulose as a ion of activation enthalpy.

for α mode was described in previous work [11]. In Fig. 6, we displayed this phenomenon by aligning the energy activation values. We observed that the compensation phenomenon was more extended for dried cellulose. The energy activation values was upper than 350 kJ mol^{-1}. It is almost two times higher than ones obtained for pristine cellulose. So the size of mobile sequences involved in α relaxation for dried cellulose is longer than for hydrated cellulose. The increase of length of the relaxant entities depend on the decrease of density of hydrogen bonds related to water departure.

4. Discussion

The influence of hydration on cellulose molecular mobility was investigated by two dielectric methods: DDS and TSC. The results of hydrated and dried samples were compared. Four relaxation modes were observed for pristine cellulose (maintained at 4 °C). For dried cellulose (24 h under vacuum at 120 °C) only three modes were pointed out. The isothermal mode (at 35 °C) related to a first order transition disappeared after dehydration. At lower temperature, two relaxation modes, γ and β, were exhibited. DDS analysis shows that comparing to dried sample, the energy activation value increases for hydrated sample. By TSC, the maximum of the γ relaxation peak appears at lower temperature after dehydration. Then the mobility of side groups (assigned to γ mode) for dried cellulose increases. For hydrated sample the water–polymer hydrogen bonds decreases the hydroxyl and hydroxymethyl mobility forming the water–polymer complex (larger volume and inertia). The water molecules have an anti-plasticizer effect on the γ mode.

For β relaxation mode only recorded by TSC experiment, a different behavior was observed. The hydration plays a role of plasticizer for this relaxation mode. The water molecules disrupt pre-existing hydrogen bonds, increasing the open space between the polymer chains and reducing the hindrance for the local chain mobility. Consequently, the activation energy value was lower for the β mode of hydrated sample.

At higher temperature, the α relaxation mode was observed by both DDS and TSC methods. It is assigned to the dielectric manifestation of the glass transition corresponding to delocalized cooperative molecular mobility of long chain segments of cellulose. Upon hydration, DDS shows a lowering of the average activation energy. Such an effect has been assigned to the localization of the molecular mobility inherent with an increase of the density of hydrogen bonds due to interactions with water molecules. By TSC, the wide range of activation enthalpy observed in dried cellulose (Fig. 6) is significantly restricted upon hydration. This evolution confirms the hypothesis of additional hydrogen bonds with water molecules resulting in a restriction of the length of mobile units.

5. Conclusion

The synergy between two dielectric methods allowed us to investigate on a wide frequency and temperature scale the influence of hydration on cellulose molecular mobility. The dielectric γ and β relaxation modes were located in the low temperature range. The mobility of side groups, assigned to γ mode, for dried cellulose increased. The water molecules had an anti-plasticizer effect on γ mode due to water–polymer hydrogen bonding with the hydroxyl and hydroxymethyl entities. For β relaxation mode, observed only by Thermo Stimulated Current experiments, the hydration plays a role of plasticizer for this relaxation mode due to a free volume effect. The dielectric α relaxation mode was located in the high temperature range. The α relaxation mode assigned to delocalized cooperative movements of long chain segments was shifted towards lower temperatures due to a decrease of the activation energy. By Thermo Stimulated Current, the wide range of activation enthalpy observed in dehydrated cellulose is also significantly decreased upon hydration. This evolution has been assigned to an increase of the hydrogen bonds density leading to a more localized cooperative mobility.

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